EFFECTS OF COMPATIBILIZER ON MORPHOLOGY, MECHANICAL AND THERMAL PROPERTIES OF POLYLACTIC ACID/NATURAL RUBBER BLEND

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A thesis submitted in fulfillment of the
requirements for the award of the degree of
Master of Engineering (Polymer)

Faculty of Chemical & Energy Engineering
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DECEMBER 2015

"I dedicate this entire work to my beloved parents, sisters and younger brother..
Thanks for the love and support"

ACKNOWLEDGEMENT

In the name of Allah, the Most Beneficent and the Most Merciful. All praises to Allah the Almighty for giving me the strengths, guidance and patience in completing this thesis. With His blessing, this thesis is finally accomplished.

First of all I would like to express my genuine gratitude to my supervisor Dr Agus bin Arsad and P.M. Dr. Abdul Razak bin Rahmat for their support and encouragement during period of my studies. Your practical view and guidance on my research work was of the utmost importance. Thank you very much for the unending help throughout the course of my research.

My sincere thanks to my beloved parents, Mr. Hj. Abdullah Sani Bin Ramli and Mrs. Hjh. Marbiah Bte Mohamad for their endless love, prayers and tolerance. To my wonderful sisters and younger brother, thank you for your persevering support and encouragement.

A special appreciation towards all my beloved friends, Shaifful Shazmie, Nor Nisa Balqis, Nurul Husna, Siti Najihah, Nurul Ain, Nur Azmyra, Noora'tiqah, Mohd Shaiful Zaidi and Muhamad Rasyidi for giving their everlasting support towards me through thick or thin and being there for me when I needed them the most. Not forgetting to thank the staff of Polymer Engineering Department of Faculty of Chemical Engineering especially Mr Izat, Mr Suhee and Miss Zainab for helping me throughout the research. Without those helps, there would be no possibility for this thesis to be completed. Thank you.

ABSTRACT

The primary focus of this study was to prepare two types of compatibilizers, i.e. polylactic acid-grafted-maleic anhydride (PLA-g-MA) and natural rubber-grafted-maleic anhydride (NR-g-MA) for PLA/NR blends. In the first phase of the study, PLA/NR blends with different NR concentration in the range of 5 to 20 wt% were fabricated. Experimental results showed that PLA/NR blend containing 5 wt% of NR concentration (designated as PLA95/NR5) was the optimum blend due to its higher impact strength (35.74 J/m) and elongation at break (1.84%) as compared to other PLA/NR blends. In the second phase of the study, the two types of compatibilizers (PLA-g-MA and NR-g-MA) with different MA concentrations in the range of 3 to 12 phr were prepared using melt grafting free-radical polymerization method. It was found that the optimum MA concentration for grafting PLA and NR were both 9 phr with the degree of grafting of 1.63% and 5.02%, respectively. In the third phase, the PLA95/NR5 blend was incorporated with different compatibilizers (PLA-g-MA and NR-g-MA) at various loadings (1-10 phr). The experimental results of the mechanical properties, i.e. impact strength, elongation at break and storage modulus of the PLA95/NR5 blend did not show significant enhancement upon addition of PLA-g-MA in the blend. Scanning electron microscope results showed better interfacial adhesion between PLA and NR phases upon addition of 3 phr PLA-g-MA into the blend. The improvement in the interfacial adhesion of the blend could be attributed to the good dispersion of the NR particles in the PLA matrix with the aid of PLA-g-MA compatibilizer. On the contrary, the addition of NR-g-MA did not show much improvement in the mechanical properties of the PLA95/NR5 blend but thermal stability of the blend was increased as compared to the PLA95/NR5. In all tests, further increased of PLA-g-MA and NR-g-MA up to 5 phr and 10 phr, respectively in the PLA95/NR5 blend caused the blend stiffness to increase. This possibly due to an increase in the amount of MA and the reduction of NR elasticity.

ABSTRAK

Fokus utama kajian ini adalah untuk menyediakan dua jenis penserasi, iaitu asid polilaktik-cantuman-maleik anhidrida (PLA-g-MA) dan getah asli-cantuman-maleik anhidrida (NR-g-MA) untuk campuran PLA/NR. Pada fasa pertama kajian ini, campuran PLA/NR dengan kepekatan NR yang berbeza-beza dalam julat antara 5 hingga 20% berat telah direka. Hasil kajian mendapati bahawa campuran PLA/NR dengan kepekatan NR sebanyak 5% berat (ditetapkan sebagai PLA95/NR5) adalah gabungan optimum kerana mempunyai kekuatan hentaman (35.74 J/m) dan pemanjangan pada takat putus (1.84%) yang lebih tinggi berbanding campuran PLA/NR yang lain. Pada fasa kedua kajian, dua jenis penserasi (PLA-g-MA dan NR-g-MA) dengan kepekatan MA yang berbeza-beza dalam julat antara 3 hingga 12 phr telah disediakan menggunakan kaedah pempolimeran cantuman leburan radikal bebas. Keputusan kajian mendapati bahawa kepekatan optimum MA bagi cantuman PLA dan NR adalah masing-masing sebanyak 9 phr dengan darjah cantuman adalah 1.63% dan 5.02%. Pada fasa ketiga kajan, campuran PLA95/NR5 telah digabungkan dengan penserasi (PLA-g-MA dan NR-g-MA) dengan muatan yang berbeza-beza (1-10 phr). Keputusan eksperimen sifat-sifat mekanik, iaitu kekuatan hentaman, pemanjangan pada takat putus dan modulus penyimpanan campuran PLA95/NR5 tidak menunjukkan peningkatan yang ketara dengan penambahan PLA-g-MA di dalam campuran tersebut. Hasil pengimbasan mikroskop elektron menunjukkan bahawa lekatan antara muka di antara fasa PLA dan NR menjadi lebih baik dengan penambahan 3 phr PLA-g-MA ke dalam campuran tersebut. Peningkatan pada lekatan antara muka campuran tersebut boleh dikaitkan dengan penyebaran partikel NR yang baik dalam matriks PLA dengan bantuan penserasi PLA-g-MA. Sebaliknya, penambahan NR-g-MA tidak menunjukkan banyak peningkatan pada sifat mekanikal campuran PLA95/NR5 tetapi kestabilan haba campuran telah meningkat berbanding dengan PLA-g-MA. Dalam kesemua ujian, penambahan PLA-g-MA dan NR-g-MA masing-masing sehingga 5 phr dan 10 phr ke dalam campuran PLA95/NR5 menyebabkan kekakuan campuran akan meningkat. Ini mungkin disebabkan oleh peningkatan jumlah MA dan pengurangan keanjalan NR.

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LIST OF ABBREVIATION

AEM	-	Ethylene-acrylic rubber
BPO	-	Benzoyl peroxide
DMA	-	Dynamic Mechanical Analysis
DSC	-	Differential Scanning Calorimetry
DTG	-	Derivative Thermogravimetric
EGMA	-	Poly(ethylene-glycidyl methacrylate)
ENR	-	Epoxidized natural rubber
EPM	-	Ethylene-propylene copolymer
FTIR	-	Fourier Transform Infrared Spectroscopy
GMA	-	Glycidyl methacrylate
HBP	-	Hyperbranched poly(ester amide)
HDPE	-	High density polyethylene
^{1}H-NMR	-	Proton Nuclear Magnetic Resonance
IR	-	Isoprene rubber
LGM	-	Lembaga Getah Malaysia
MA	-	Maleic anhydride
MAPLA	-	Maleated polylactide
NBR	-	Nitrile-butadiene rubber
NR	-	Natural rubber
NR-g-MA	-	Natural rubber-grafted-maleic anhydride
PCL	-	Polycaprolactone
PE	-	Polyethylene
PET	-	Poly(ethylene terephthalate)
phr	-	Part per hundred resin

PLA	-	Polylactic acid
PLA-g-MA	-	Polylactic acid-grafted-maleic anhydride
PMMA	-	Poly(methyl methacrylate)
PP	-	Polypropylene
PS	-	Polystyrene
PVAc	-	Poly(Vinyl Acetate)
SEM	-	Scanning Electron Microscope
SNR	-	Styrene-based deproteinized natural rubber
TGA	-	Thermogravimetric Analysis
TPEE	-	Thermoplastic polyester elastomer
TPS	-	Thermoplastic starch
TPU	-	Thermoplastic polyurethane
ULDPE	-	Ultra low density polyethylene

LIST OF SYMBOLS

E'	-	Storage modulus
E"	-	Loss modulus
g/cm^3	-	gram per centimeter cube
GPa	-	Giga Pascal
J/m	-	Joule per meter
kJ/m^2	-	kiloJoule per meter square
ml	-	milliliter
MPa	-	Mega Pascal
rpm	-	revolution per minute
Tan δ	-	Tangent delta
T_{cc}	-	Cold crystallization temperature
T_g	-	Glass transition temperature
T_m	-	Melting temperature
T_{max}	-	Maximum temperature
T_{onset}	-	Onset temperature
w/w	-	Weight per weight
wt%	-	Weight percentage
X_c	-	Degree of crystallinity
ΔH_f	-	Heat of fusion
μm	-	Micrometer

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Plastic materials produced from petrochemicals has became a great used in packaging, automotive, healthcare application, and communication or electronic industries. As these conventional synthetic polymers are not easily degraded because of their high molecular mass and hydrophobic character, may accumulate in the environment and represent a significant source of environmental pollution potentially harming wildlife. One of the possible solutions to this problem is to replace the petroleum-based plastic with the biodegradable polymers with suitable mechanical and physical properties which have received particular attention. A necessary prerequisite for extending their utilization is their biodegradability in natural environments, which may serve as a source of carbon and energy for a variety of microorganisms.

Polylactic acid (PLA) is known as a biodegradable thermoplastic polymer with wide range of potential application such as disposable packaging, medical implants, textiles and automobile industries (Phruksaphithak and Noomhorm, 2012). The PLA has attracted industrial community's attention because its starting material, lactic acid, is obtained by a fermentation process from 100% renewable resources. Conventional methods to process PLA are extrusion, injection moulding, blow moulding and thermoforming. The PLA is available in a form of rigid or flexible and have advantages in terms of eco-friendly, biocompatibility, processibility and energy

savings. However, there are some drawback of PLA such as too stiff and brittle for room temperature applications, slow degradation rate, hydrophobic nature and lack of reaction side-chain groups (chemically inert) have become major obstacles for expanding its applications as a common plastic material (Rasal *et al.,* 2010). Several stratergies have been attempted to overcome these problems, for instance improving mechanical properties by chemical modification through copolymerization and surface modification (Xiao *et al.,* 2012). However, both of these approaches show some limitation in mechanical properties of PLA. The chemical modification in large scale requires expensive equipment and increase in brittleness still remains a problem to be solved. Meanwhile, the surface modification was only focused on biomedical applications of PLA.

Another practical strategy to overcome these drawbacks is by combining PLA with other polymers to create a polymer material with different physical properties (Thomas *et al,* 2015). This method, so-called polymer blending, has utilised various of synthetic polymers as a second polymer. These include poly(ethylene) (Anderson *et al.,* 2003), polycaprolactone (Wu *et al.,* 2008), poly(butylene succinate) (Yokohara and Yamaguchi, 2008) and poly(vinyl acetate) (Gajria *et al.,* 1999). In general, these blends showed considerably higher toughness than pure PLA. However, these polymers are petroleum based and need to be replaced with biodegradable polymer to minimize negative impact to environment. Therefore, new material from renewable resource such as natural rubber (NR) has attracted much attention as possible second phase polymer, mainly due to its renewability and recovery properties. NR is known to have high molecular weight and very low glass transition temperature about -70°C compared to other synthetic polymer materials. Its excellent properties in terms of mechanical strength, resilience, elongation at break and low cost make NR a remarkable polymer as PLA toughening agent (Wongsorat *et al.*, 2010).

The polymer blend represents a very important field in polymeric materials, which offers better properties in comparison with the neat polymers. It has been reported that the final properties of the polymer blends are related to the quality of their morphology, which in turns depends on a rheological properties of components

of the blend, composition of the blend, processing conditions used to obtain the blend, and the compatibility between the polymers forming the blend (Thomas *et al.,* 2015). Among them, the most important controlling parameter in polymer blend processes is degree of compatibility of the blended polymers (Nawaz *et al.,* 2010). However, literatures reveals that most polymer blends are incompatible, resulting in materials with coarse morphology, weak adhesion among phases and poor mechanical properties. The compatibility between the polymers of a blend can be improved by the addition of compatibilizers which results in a finer and more stable morphology, better adhesion between the polymers of the blend and consequently better properties of the final product.

1.2 Problem Statement

The major drawbacks of PLA are its low elongation at break, impact strength, heat deflection temperature and low melt strength. One way to overcome the brittleness of PLA is through polymer blending. In this research work, NR was selected as second polymer phase for PLA. According to Bitinis *et al.* (2011), the ductility of PLA can be improved by blending with NR due to its high specific strength and modulus, low density, renewability and high elongation at break. However, the difference in the polarity and molecular weight of PLA and NR may also result in poor compatibility and led to poor mechanical properties of the blend. Thus, the compatibility between PLA and NR need to be improved. In this study, a third component called compatibilizer was prepared and used to increase the interaction between the PLA and NR. Two types of compatibilizers were prepared and used which were NR-g-MA and PLA-g-MA. These two compatibilizers were synthesized by melt grafting free-radical polymerization method using maleic anhydride (MA) as a monomer. MA was grafted onto PLA and NR during melt mixing in the presence of benzoyl peroxide (BPO) as an initiator using an internal mixer.

MA was selected in this study due to its good chemical reactivity, low toxicity and low potential to polymerize itself under free radical grafting conditions. In addition, MA was considered for the present study based on the extensive use of grafting MA or maleic copolymers as a compatibilizer in binary immiscible polymer blends as reported by Carone *et al.* (2000), Zhang and Sun (2004) and Teamsinsungvon *et al.* (2012). Hence, it is expected that the incorporation of compatibilizers into PLA/NR blend could enhance the interaction between these two polymers as well as mechanical properties of the blend.

1.3 Objectives of Research

The objectives of this study are:

i. To study the influence of NR concentration on the mechanical, thermal and morphology properties of PLA/NR blends.

ii. To synthesize and characterize PLA-g-MA and NR-g-MA compatibilizers.

iii. To investigate the influence of compatibilizers loading on the mechanical, thermal and morphology properties of PLA/NR blends.

1.4 Scope of Research

In order to achieve the objectives of the research, following scopes of work have been performed:

(i) Preparation of PLA/NR blends using four different concentrations of NR ranging from 5 to 20 wt% via melt blending method using a twin screw extruder. Then, the blends were moulded using hot press moulding.

(ii) Investigation on the effect of NR concentration on the morphology, mechanical and thermal properties of the PLA/NR blend and identification of the ideal NR concentration for preparing PLA/NR blend.

(iii) Synthesis of NR-g-MA and PLA-g-MA compatibilizers using melt grafting free-radical polymerization and MA as a monomer.

(iv) Characterization of the compatibilizers using direct titration method, Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (^{1}H-NMR) in order to determine the degree of grafting and to confirm the existence of MA on PLA structure.

(v) Preparation of polymer blends by using different concentrations of compatibilizer (1 to 10 phr) in the PLA containing 5 wt% NR blend and determination of its mechanical properties using tensile test, flexural test and Izod impact test.

(vi) Characterization of the polymer blend structure and morphology using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM), respectively.

(vii) Determination of the thermal degradation behaviour using thermogravimetric analysis (TGA), investigation of the thermal and dynamic mechanical properties of the blends using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), respectively.

(viii) Identification of the optimum amount of compatibilizer for PLA/NR blend based on their morphology, mechanical and thermal properties.

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